Liquid-Liquid Equilibria of Water + Propionic Acid + Methyl Butyl Ketone and of Water + Propionic Acid + Methyl Isopropyl Ketone

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Abstract

Experimental liquid-liquid equilibria of water + propionic acid + methyl butyl ketone and of water + propionic acid + methyl isopropyl ketone systems were investigated at temperatures 25, 35 and 45 °C. Complete phase diagrams were obtained by evaluating the solubility and the tie-line data. The reliability of the experimental tie-line data was determined through the Othmer-Tobias plots. Distribution coefficients and separation factors were evaluated over the immiscibility regions. It is concluded that both the high boiling solvents are suitable separating agent for dilute aqueous propionic acid.

Keywords: liquid-liquid equilibria, solvent extraction, propionic acid, ternary system.

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Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes is important, and many solvents have been tried to improve such recovery[1-5]. Propionic acid is being used as cellulosic solvents in pharmaceutical industries and also can be used to provide propionates, which are used as fungicides[6]. It is also used in electroplating industry and to prepare perfume esters. Precise liquid-liquid equilibrium data are required for extraction processes. The objective of this work is to determine the experimental solubility and the tie-line data of water + propionic acid + methyl butyl ketone and of water + propionic acid + methyl isopropyl ketone at various temperatures. Complete phase diagrams were obtained by evaluating the solubility and the tie-line data simultaneously for each ternary system. In addition, the thermodynamic consistency of the tie-line data was ascertained by making the Othmer-Tobias plots[7]. In order to compare the selectivity advantages of methyl butyl ketone and methyl isopropyl ketone, solvent free-based selectivity diagrams were plotted.

Experimental Section

Chemicals. Propionic acid (99.99%), methyl butyl ketone and methyl isopropyl ketone (99%) were purchased from Merck. The propionic acid was redistilled with the middle 80% collected. An Abbe refractometer were used to measure the refractive indices at the studied temperatures. A Westphal apparatus measured the densities at the same temperatures. The solvents were also redistilled under a moderate vacuum, with approximately the middle 70% collected. Deionized water was used during the experiments.

Procedure. The tie line data determination was performed in an equilibrium cell equipped with magnetic stirrer and isothermal fluid jacket. The mixtures temperatures

were regulated by a thermostatic bath with an accuracy of ± 0.1°C. The inner temperature of the cell was measured with an accuracy of ± 0.1°C by a certified Fischer thermometer. The cell designed to contain a solution of 200 cm^3, was filled with homogeneous water + acid + solvent mixtures prepared by weighing. An electronic balance, accurate to ± 0.1 mg was used during the experiments. The solvent was added by means of an automated microburet with an accuracy of ± 0.005 cm^3. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture.

Results and Discussion

The experimental tie lines and data of water (1) + propionic acid (2) + methyl butyl ketone (3) and of water (1) + propionic acid (2) + methyl isopropyl ketone (3) ternaries at 25, 35 and 45° C are presented in Tables 1-6 respectively. The results show that the solubility of the two high boiling solvents is good for the propionic acid. It is also concluded that both solvents show extremely low solubilities against water and can be used to extract the propionic acid from its dilute aqueous solutions. To show the selectivity and strength of the solvents to extract the acid, distribution coefficients Di for the propionic acid (i=2) and separation factor S are determined as follows:

$$D_i = \frac{W_{i3}}{W_{i1}} \quad (1)$$

$$S = \frac{D_2}{D_1} \quad (2)$$

W_{i3} and W_{i1} are the mass fractions in the solvent and aqueous phase, respectively. The results for the system of of water (1) + propionic acid (2) + methyl butyl ketone (3) and of water (1) + propionic acid (2) + methyl isopropyl ketone (3) ternaries at 25° C are listed in Tables 7 and 8. The results for the distribution function make the solvents

a good candidate as a separating agent. The typical solubility curve for the system of water (1) + propionic acid (2) + methyl butyl ketone (3) at 25 and 35° C, obtained from the tie-line data are presented as figures 1 and 2. Again, it is inferred that the solvent is considered as a suitable agent in extraction of propionic acid. The reliability of the experimentally measured tie-line data is determined by making the Othmer Tobias plots for each ternary. Going through the figure 3 the linearity of the plot indicates the degree of consistency of the related data. Similar results are observed for the rest of data. In order to compare the selectivity advantages of methyl butyl ketone and methyl isopropyl ketone, solvent free-based selectivity diagrams were plotted as figure 4.

Conclusions

The experimental tie line data have been measured to show the miscibility and immiscibility regions for the ternary systems of water (1) + propionic acid (2) + methyl butyl ketone (3) and of of water (1) + propionic acid (2) + methyl isopropyl ketone (3). The data have been collected and reported at atmospheric pressure and at 25, 35 and 45°C respectively.

It is concluded that both solvents, showing extremely low solubilities against water, may serve as adequate solvents to extract propionic acid from its dilute aqueous solutions. Another noteworthy observation is that the complete break of conjugate phases was never hindered by density, viscosity and interfacial tension related phenomenon during the settling process.

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Captions for figures:

Figure 1. Ternary diagram for experimental liquid-liquid equilibria (LLE) of water (1) + propionic acid (2) + methyl butyl ketone (3), at 25°C. •: tie-line data; —— : solubility curve.

Figure 2. Ternary diagram for experimental liquid-liquid equilibria (LLE) of water (1) + propionic acid (2) + methyl butyl ketone (3), at 35°C. •: tie-line data; —— : solubility curve.

Figure 3. Othmer Tobias plot for water (1) + propionic acid (2) + methyl butyl ketone (3), at 25°C.

Figure 4. Selectivity diagram for both ternaries at 25°C. ●: of water (1) + propionic acid (2) + methyl butyl ketone (3); ▲: water (1) + propionic acid (2) + methyl isopropyl ketone (3).

Table 1. Tie-line data for water (1) + propionic acid (2) + methyl butyl ketone (3), at 25°C.

	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9980	0.0000	0.0020	0.1100	0.0000	0.8900
	0.9946	0.0028	0.0026	0.1513	0.0400	0.8087
	0.9913	0.0061	0.0026	0.1829	0.0751	0.7420
	0.9853	0.0080	0.0027	0.2033	0.1033	0.6934
	0.9837	0.0133	0.0030	0.2496	0.1504	0.6000
25°C	0.9799	0.0163	0.0038	0.2846	0.1844	0.5310
	0.9725	0.0235	0.0040	0.3192	0.2155	0.4653
	0.9623	0.0336	0.0041	0.3645	0.2553	0.3802
	0.9526	0.0432	0.0042	0.4450	0.2760	0.2790
	0.9433	0.0517	0.0050	0.4993	0.2786	0.2221
	0.9193	0.0705	0.0102	0.6000	0.2520	0.1480
	0.8948	0.0881	0.0171	0.6849	0.2201	0.0950

Table 2. Tie-line data for water (1) + propionic acid (2) + methyl butyl ketone (3), at 35°C.

	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9970	0.0000	0.0030	0.1098	0.0000	0.8902
	0.9938	0.0024	0.0038	0.1488	0.0361	0.8171
	0.9920	0.0040	0.0040	0.1740	0.0630	0.7630
	0.9871	0.0081	0.0048	0.1994	0.1031	0.6975
	0.9849	0.0101	0.0050	0.2197	0.1260	0.6543
35°C	0.9815	0.1330	0.0052	0.2491	0.1552	0.5957
	0.9762	0.0182	0.0056	0.2849	0.1904	0.5247
	0.9700	0.0244	0.0056	0.3217	0.2163	0.4620
	0.9643	0.0300	0.0057	0.3626	0.2403	0.3969
	0.9566	0.0361	0.0073	0.4068	0.2588	0.3344
	0.9452	0.0466	0.0082	0.4827	0.2720	0.2453
	0.9442	0.0548	0.0100	0.5394	0.2560	0.1946
	0.9257	0.0732	0.0110	0.6117	0.2475	0.1408

Table 3. Tie-line data for water (1) + propionic acid (2) + methyl butyl ketone (3), at 45°C.

	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9970	0.0000	0.0030	0.1348	0.0000	0.8652
	0.9934	0.0028	0.0038	0.1648	0.0381	0.7971
	0.9910	0.0050	0.0040	0.1900	0.0660	0.7440
	0.9872	0.0082	0.0046	0.2297	0.1091	0.6522
	0.9850	0.0100	0.0050	0.2491	0.1316	0.5193
	0.9804	0.0142	0.0054	0.2842	0.1622	0.5533
45°C	0.9763	0.0182	0.0055	0.3145	0.1865	0.4990
	0.9703	0.0240	0.0057	0.3530	0.2085	0.4385
	0.9597	0.0323	0.0080	0.3921	0.2283	0.3796
	0.9450	0.0461	0.0083	0.4647	0.2522	0.2831
	0.9302	0.0600	0.0098	0.5147	0.2563	0.2190
	0.9262	0.0721	0.0170	0.5790	0.2443	0.1767

Table 4. Tie-line data for water (1) + propionic acid (2) + methyl isopropyl ketone (3), at 25°C.

	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9925	0.0000	0.0075	0.1886	0.0000	0.8114
	0.9858	0.0029	0.0113	0.2190	0.0403	0.7407
	0.9821	0.0066	0.0113	0.2630	0.0722	0.5648
25°C	0.9780	0.0106	0.0114	0.3109	0.1080	0.5811
	0.9744	0.0142	0.0114	0.3610	0.1320	0.5070
	0.9674	0.0206	0.0120	0.4170	0.1714	0.4116
	0.9542	0.0300	0.0158	0.4976	0.1921	0.3103

Table 5. Tie-line data for water (1) + propionic acid (2) + methyl isopropyl ketone (3), at 35°C.

	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9920	0.0000	0.0080	0.1893	0.0000	0.8107
	0.9887	0.0028	0.0085	0.2173	0.0331	0.7496
	0.9849	0.0066	0.0085	0.2721	0.0754	0.5525
35°C	0.9812	0.0103	0.0085	0.3234	0.1069	0.5897
	0.9750	0.0140	0.0110	0.3599	0.1300	0.5101
	0.9688	0.0200	0.0112	0.4262	0.1676	0.4062
	0.9580	0.0304	0.0116	0.5048	0.1953	0.2999

Table 6. Tie-line data for water (1) + propionic acid (2) + methyl isopropyl ketone (3), at 45°C.

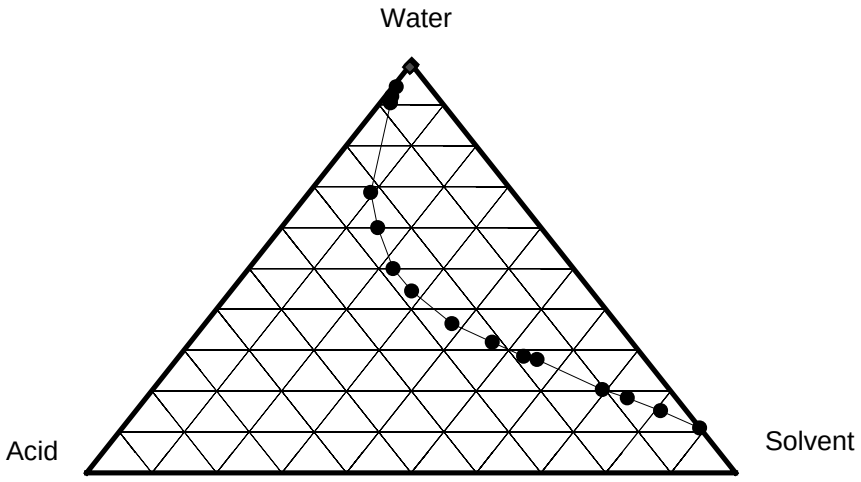
	Aqueous Phase			Organic Phase		
	X1	X2	X3	X1	X2	X3
	0.9920	0.0000	0.0080	0.1921	0.0000	0.8079
	0.9884	0.0031	0.0085	0.2410	0.0425	0.7155
	0.9845	0.0065	0.0090	0.2880	0.0775	0.5345
45°C	0.9787	0.0123	0.0090	0.3300	0.1100	0.5600
	0.9755	0.0150	0.0095	0.3750	0.1330	0.4920
	0.9700	0.0200	0.0100	0.4500	0.1675	0.3825
	0.9610	0.0260	0.0130	0.5200	0.1803	0.3000

Table 7. Mass fraction distribution coefficients D_i of water (1) + propionic acid (2) + methyl butyl ketone (3), at 25°C.

D_2	D_1	S
14.287	0.1521	93.909
12.311	0.1845	66.726
12.912	0.2063	62.580
11.308	0.2537	44.567
11.312	0.2904	38.951
9.1702	0.3282	27.938
7.5982	0.3787	20.059
6.3888	0.4671	13.676
5.3887	0.5293	10.180
3.5744	0.6526	5.4766
2.4982	0.7654	3.2639

Table 8. Mass fraction distribution coefficients D_i of water (1) + propionic acid (2) + methyl isopropyl ketone (3), at 25°C.

D_2	D_1	S
13.896	0.2221	62.553
10.939	0.2677	40.850
10.188	0.3178	32.050
9.2957	0.3704	25.090
8.3203	0.4310	19.302
6.4033	0.5214	12.279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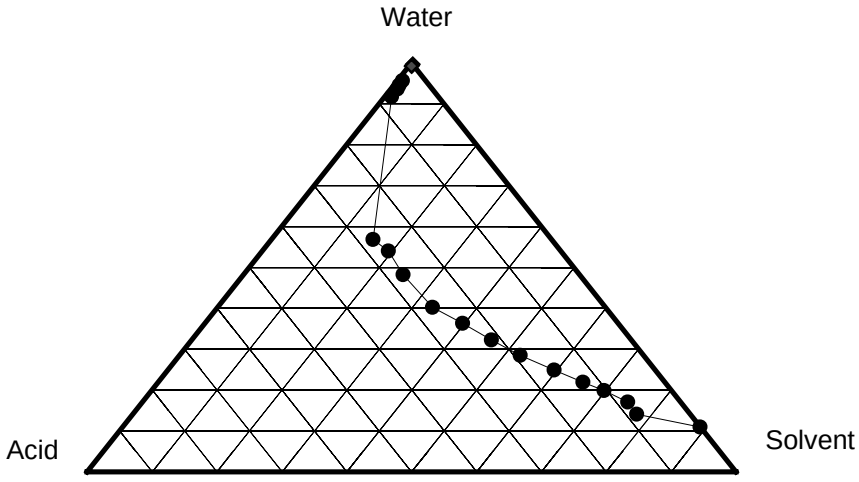
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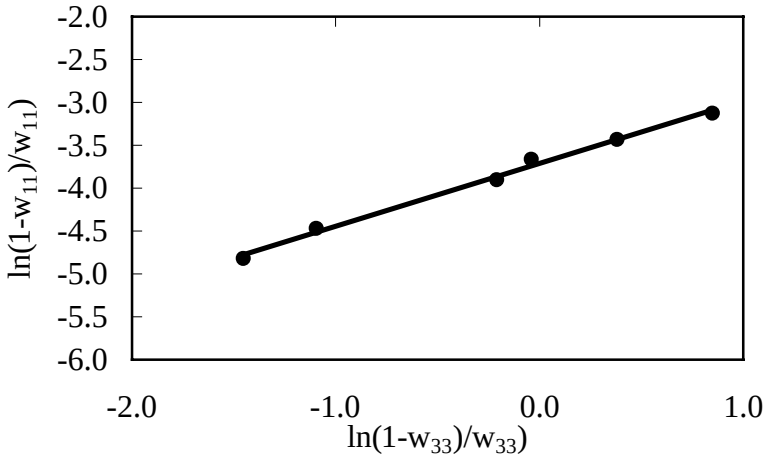
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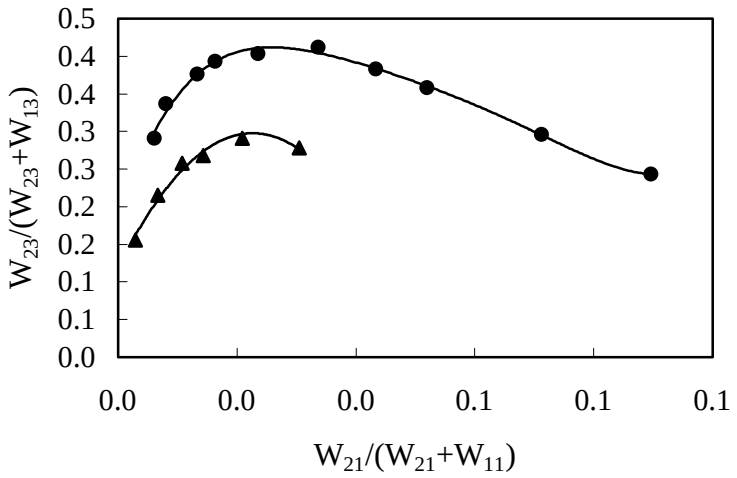
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